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AD-A232 208

CUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) PL-TR-91-2041			7a. NAME OF MONITORING ORGANIZATION DTIC ELECTE		
6a. NAME OF PERFORMING ORGANIZATION Phillips Lab, Geophysics Directorate		6b. OFFICE SYMBOL (if applicable) LID	7b. ADDRESS (City, State, and ZIP Code) Hanscom AFB Massachusetts 01731-5000		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO 61102F	PROJECT NO 2310	TASK NO G3
			WORK UNIT ACCESSION NO 20		
11. TITLE (Include Security Classification) Rate Constant and Branching Fraction for the Reaction of $O^+(^2D, ^2P)$ with CO_2					
12. PERSONAL AUTHOR(S) A.A. Viggiano, Robert A. Morris, John F. Paulson					
13a. TYPE OF REPORT Reprint		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 1991 February 21	
15. PAGE COUNT 2					
16. SUPPLEMENTARY NOTATION Reprinted from J.Chem. Phys. 93(2) 15 July 1990					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Ion-molecule reactions, Charge transfer, Monitor ion technique		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Rate constants for the reactions of $O^+(^2D)$ and $O^+(^2P)$ with CO_2 have been measured and are both found to be the same as measured earlier for the reaction of the ground state of O^+. However, the product ion in the reactions of the given excited electronic states is CO_2^+, i.e., the reaction proceeds by charge transfer, or perhaps by ion-atom interchange rather than by oxygen atom abstraction, as in the reaction of the ground electronic state of O^+ with CO_2 at low translational energy.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL J.F. Paulson			22b. TELEPHONE (Include Area Code) (617) 377-3124		22c. OFFICE SYMBOL LID

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SECURITY CLASSIFICATION OF THIS PAGE
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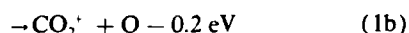
Rate constant and branching fraction for the reaction of $O^+(^2D,^2P)$ with CO_2

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(Received 21 March 1990; accepted 5 April 1990)

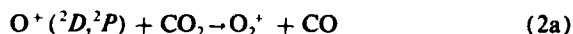
The reaction



has been extensively studied.¹⁻¹² Reaction (1a) is known to be fast¹² although it is spin forbidden.³ At room temperature, reaction (1b) is slow due to the endothermicity of the reaction.^{13,14} However, as the energy or temperature of the reactants is raised the charge transfer channel becomes important even though the overall rate constant changes only slightly.^{6,15,16}

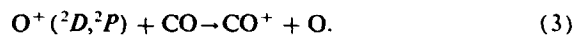
Recently, it has been determined that most of the O_2^+ produced in reaction (1a) is vibrationally excited.¹¹ This has important implications for the atmospheres of Venus and Mars as well as for chemical releases in the earth's atmosphere.¹⁶

While it is well established that kinetic energy drives the endothermic charge transfer, the influence of other forms of energy is not known. O^+ has two metastable states, $O^+(^2D)$ and $O^+(^2P)$, which are 3.3 and 5.0 eV above the ground $O^+(^4S)$ state, respectively.¹⁷ The lifetimes of both of these states are long (>5 s).¹⁸ Either state has sufficient energy to drive the charge transfer channel, which is endothermic by only 0.2 eV.^{13,14} In this Note we report the rate constant and branching ratio for the reaction of an unknown mixture of these states with CO_2 .



The measurements were performed in a selected ion flow tube incorporating a monitor ion inlet. The apparatus has been described in detail elsewhere^{19,20} and only details pertinent to the present experiment are given here. A mixture of excited states $O^+(^2D,^2P)$ and ground state $O^+(^4S)$ was formed in an electron impact ion source from CO_2 . The mixture of states is unknown. O^+ ions (all three states) were mass selected and injected into a helium buffer. The ions were carried down the flow tube by the helium and sampled by a downstream mass spectrometer.

Rate constants for $O^+(^2D,^2P)$ reacting with CO_2 were measured using the monitor ion technique.²⁰ This method involves injecting CO just in front of the sampling orifice (1 cm from the orifice). This converts the $O^+(^2D,^2P)$ ions to CO^+ by the fast reaction¹⁸



$O^+(^4S)$ does not react with CO.¹⁸ This allows monitoring of the excited state signal by converting the $O^+(^2D,^2P)$ signal, which is only a fraction of the signal at 16 daltons, into a signal that is monitored at 28 daltons. The decay of the CO^+ , which is thus proportional to the decay of the $O^+(^2D,^2P)$, was then monitored as a function of the CO_2 flow rate, and rate constants were derived in the normal manner.¹⁹ The rate constant for $O^+(^4S)$ reacting with CO_2 was also measured in the normal manner, except that CO was added upstream of the reaction region in order to eliminate $O^+(^2D,^2P)$ ions from contributing to the 16 amu ion signal.

The products from $O^+(^2D,^2P)$ reacting with CO_2 were determined as follows. The percentage of $O^+(^2D,^2P)$ in the total ion signal at 16 daltons was determined by monitoring the decay of that total ion signal as CO was added. Both He and CO are known not to quench the excited states,¹⁸ and CO is therefore a good monitor of the excited state fraction of the O^+ signal along the whole length of the flow tube. Upon addition of CO, 6% of the O^+ reacted to form CO^+ , indicating that 6% of the total O^+ signal was due to excited states. The reaction of $O^+(^4S)$ with CO_2 produces only O_2^+ at 300 K.^{9,12} Production of O_2^+ and CO_2^+ was monitored as a function of CO_2 flow rate when all O^+ states were present. The products of the excited state reaction were then determined by comparing the percentage of CO_2^+ produced to the amount of $O^+(^2D,^2P)$ determined by the CO monitor method. Mass resolution was kept low to avoid mass discrimination problems.

The overall rate constants for reactions 1 and 2 were both found to be $1.06 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The uncertainty is estimated to be $\pm 25\%$. The ratio of the rate constants is believed to be accurate to 5%. This reflects only the uncer-

tainty in measuring the decay of the ion signal as a function of the CO_2 flow. All other errors cancel since the experimental conditions were the same for both rate constant determinations. The rate constant for reaction 1 is found to be in good agreement with previous measurements which range from 0.9 to $1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.¹² The collision rate constant is $1.17 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for both reactions.²¹

When CO_2 was added to the mixture of all three states of O^+ in the flow tube, 5.7% of the product ions were CO_2^+ , the remainder being O_2^+ . This compares to a total of 6.0% of the O^+ ions in the 2D and 2P excited states. This implies that 95% of reaction 2 proceeds by charge transfer (2b). As stated above the resolution of the mass spectrometer was kept low for this determination, and therefore little mass discrimination was present. A small degree of mass discrimination may have affected this determination, which would then favor the lighter O_2^+ ion. We therefore report our finding as a lower limit, i.e., $\geq 95\%$ of the reaction proceeds by charge transfer.

It is interesting that both the ground and excited states of O^+ react with the same rate constant and that this rate constant is not quite equal to the collisional rate constant. We believe that the reactions do proceed at less than the collisional rate constant, even though our measurements are equal to the collision rate constant within experimental error. This belief is based on the fact that the rate constant for the ground state reaction has been measured by a number of groups and all of the measurements are slightly below the collision rate constant.¹² Since we found the rate constant for the excited state to be equal to that of the ground state with little uncertainty, we feel that the rate constant for the excited state is also below the collisional limit. A mechanism that would cause different O^+ states with greatly different energies and angular momenta to react with the same efficiency would probably depend only on some property of CO_2 . One possibility is an orientation effect. The answer to this question is beyond the scope of this paper.

Electronic energy in the O^+ changes the product of the reaction from 100% O_2^+ to $\geq 95\%$ CO_2^+ . The electronic

energy is more than 3 eV higher than the energy necessary to drive the endothermic charge transfer. This is in accord with the fact that kinetic energy also efficiently drives the charge transfer when enough energy is available.^{6,15,16} Based on the above, one would also expect other forms of energy to drive the charge transfer channel. Future experiments in our laboratory are designed to explore the influence of CO_2 vibrations on the branching ratio between O_2^+ and CO_2^+ in reaction 1.

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